

Thermochemical Conversion Technology

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ABSTRACT

Current research into the thermochemical production of two oxygenate fuels from biomass is described. The Thermochemical Conversion Program is divided into research on the production of methanol and mixed alcohols from syngas, and on the production of other liquid transportation fuels, including reformulated gasoline components (RGCs).

The methanol program is the more mature of the two and has a cost goal of \$0.46/gal. Research in this area focuses on cleaning and conditioning the raw syngas to make it suitable for use in current commercial methanol synthesis units. Research on mixed alcohol fuels is looking at the thermal production of ethanol and blends of alcohols from biomass. The mixed alcohol fuels offer potential performance advantages over any single alcohol fuel.

Research on other liquid transportation fuels is focused on producing RGCs from biomass. Biomass is first converted to a biocrude oil vapor, which is subsequently converted to RGCs using specialized catalysts. The objective of this effort is to produce RGCs at a cost of about \$0.85/gal.

The two thermochemical processes are radically different. In syngas production, the chemical reactions are operated close to thermodynamic equilibrium and are based on well-established technology. However, biocrude oil vapor is produced by a new non-equilibrium thermal technology called fast pyrolysis, in which the formation of the biocrude vapors is controlled by the time and temperature of reaction kinetics to give the desired products. These two strategies are summarized in Figure 1.

METHANOL

Methanol is produced from syngas obtained by gasifying biomass. This gasification produces a medium- or high-Btu synthesis gas rich in hydrogen and carbon monoxide, which is then catalytically converted into methanol. Production of the synthesis gas is accomplished by thermal gasification. The

operations involved in methanol production are divided into major unit operation areas: (1) feed preparation, (2) thermal gasification, (3) synthesis gas modification, and (4) methanol synthesis, as shown in Figure 2.

The U.S. Department of Energy (DOE) Office of Conservation and Renewable Energy has supported the development of biomass gasification for a number of years. Gasifier development has included air, oxygen, and indirect gasification. Air/oxygen gasifier development is currently being funded by the Office of Utility Technologies. Recent studies by Chem Systems and the National Renewable Energy Laboratory (NREL, formerly the Solar Energy Research Institute) have indicated that indirectly heated gasifiers may be competitive with oxidative heating systems. Evaluations are being performed with funding from the Office of Transportation Technologies.

Recent studies performed by NREL have shown that methanol production economics can potentially be improved if hot gas conditioning is successfully developed. In the past three years, new tar-cracking and steam-reforming catalysts have been identified in the laboratory that can potentially improve gas conditioning for alcohol production. These concepts must be tested at a reasonable scale to maximize the chances for successful development.

Raw syngas contains large concentrations of hydrogen and carbon monoxide, but cannot be used directly because it contains significant amounts of impurities. Cleaned and conditioned syngas, however, is suitable for catalytic alcohol synthesis. The feasibility of biomass gasification to produce raw syngas has been demonstrated through DOE-sponsored work on biomass gasifiers between 1980 and 1988, and catalytic methanol synthesis is a well-established commercial technology. Catalysts for the production of mixed alcohols are being studied, but are not yet fully developed. Therefore, the primary remaining issue for advancing thermochemical biomass-to-methanol conversion is the development of a cost-effective raw syngas conditioning process.

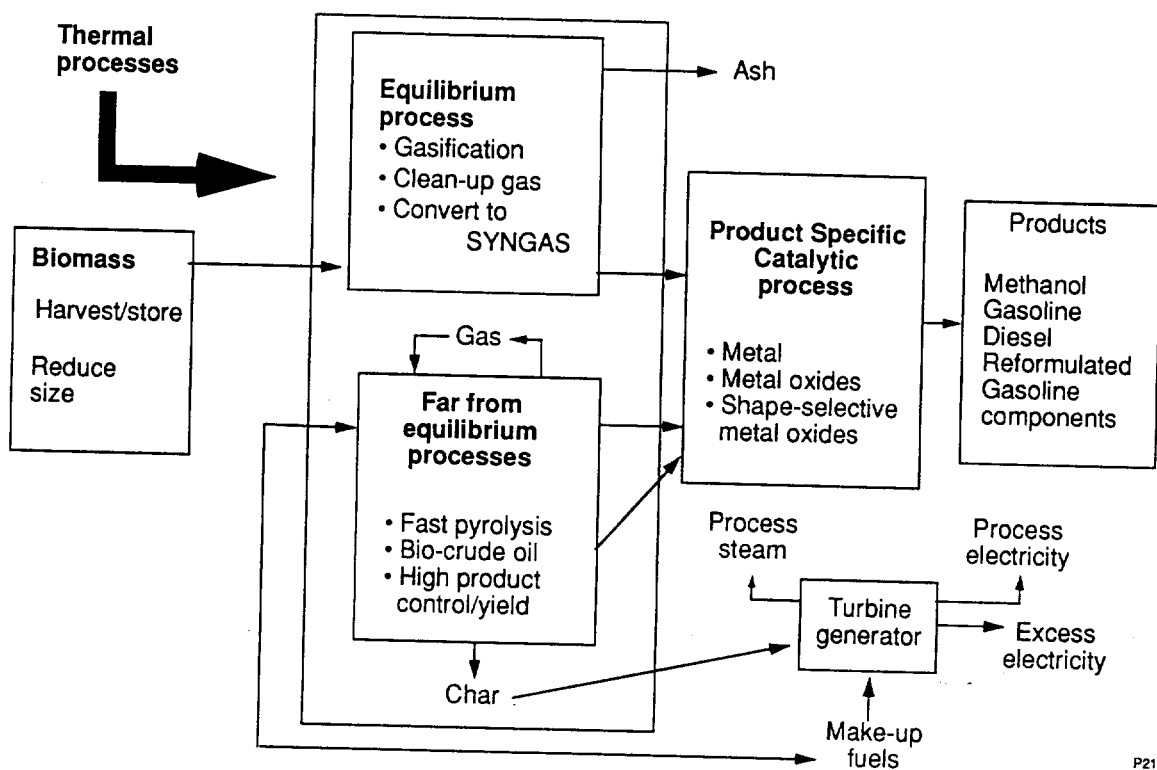


Figure 1. Thermochemical processing of biomass to fuels

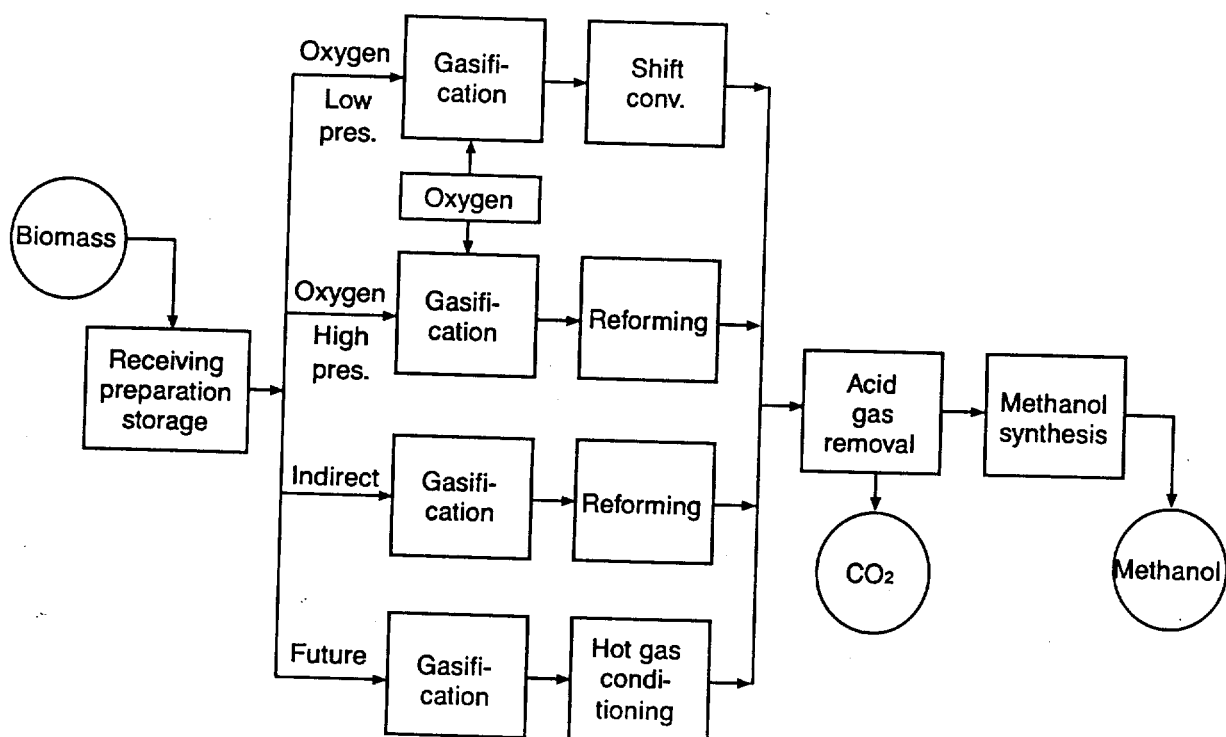


Figure 2. Thermochemical routes to methanol from biomass

Raw synthesis gas from leading biomass gasifiers contains particulate matter, methane, appreciable amounts of tar, and light hydrocarbons. It also has hydrogen to carbon monoxide ratios that are not optimum for alcohol synthesis. Because of these impurities, raw syngas does not meet feed composition requirements for methanol synthesis. Research to date in short-term experiments has shown that suitable catalysts and process technology to properly condition raw syngas are indeed possible. However, additional work is necessary to fully specify the fate of organic impurities and methane, determine the effects of major components (hydrogen, carbon monoxide, and carbon dioxide) on tar and methane removal, determine useful catalyst life, and demonstrate the suitability of catalysts to destroy tars and reduce methane under a wide variety of operating conditions. Improvements in these areas can lead to substantial savings in methanol production costs.

The NREL program of work has a major technoeconomic analysis component that is used to both integrate and guide the research, development, and demonstration (RD&D) program. NREL began a compilation of existing technoeconomic analyses on thermochemical fuels in FY 1989. In FY 1990-91 the effort was expanded to include detailed process analysis using a commercial process simulator, ASPEN/SP. This analysis has resulted in methanol production models that are consistent with those developed for ethanol. The models can be readily changed and are continually updated as new information becomes available, as shown in Figure 3 for three different gasifier types: Koppers Totzek entrained flow (K-T), IGT Renugas (IGT), and the Battelle Columbus Laboratory (BCL) indirect gasifier.

Direct syngas conditioning in one step replaces expensive quenching and scrubbing to remove tars with subsequent reheating and steam reforming to reduce excessive levels of methane. Successful completion of this research is expected to reduce methanol production costs by \$0.13-\$0.14/gal. This would bring projected methanol costs down to \$0.63/gal (1990 dollars) for a 2000-tpd (dry tons of wood per day) facility and \$0.47/gal (1990 dollars) for a 10,000-tpd facility. For comparison, the cost of methanol from natural gas is currently about \$0.40/gal. Methanol at \$0.46/gal is equivalent, on a contained energy basis, to \$0.85/gal gasoline (rack price) produced from \$25/bbl crude oil.

CURRENT STATUS - In FY 1989, NREL began research on catalysts for cracking biomass gasifier tars. This research continued in FY 1990 with the screening of several promising and/or inexpensive catalysts using a standard protocol, a laboratory tar generator, and a fixed-bed catalyst. This research used a molecular beam mass spectrometer (MBMS) interfaced with a catalytic reactor. The MBMS system allows rapid catalyst testing on a small scale and permits catalysts to be evaluated with respect to different tars produced from various biomass feedstocks at different temperatures.

The ability to study a variety of biomass-produced tars is important because tar composition can vary significantly with the severity of cracking experienced during tar generation. Raw syngas from feedstocks such as refuse-derived fuel (RDF)

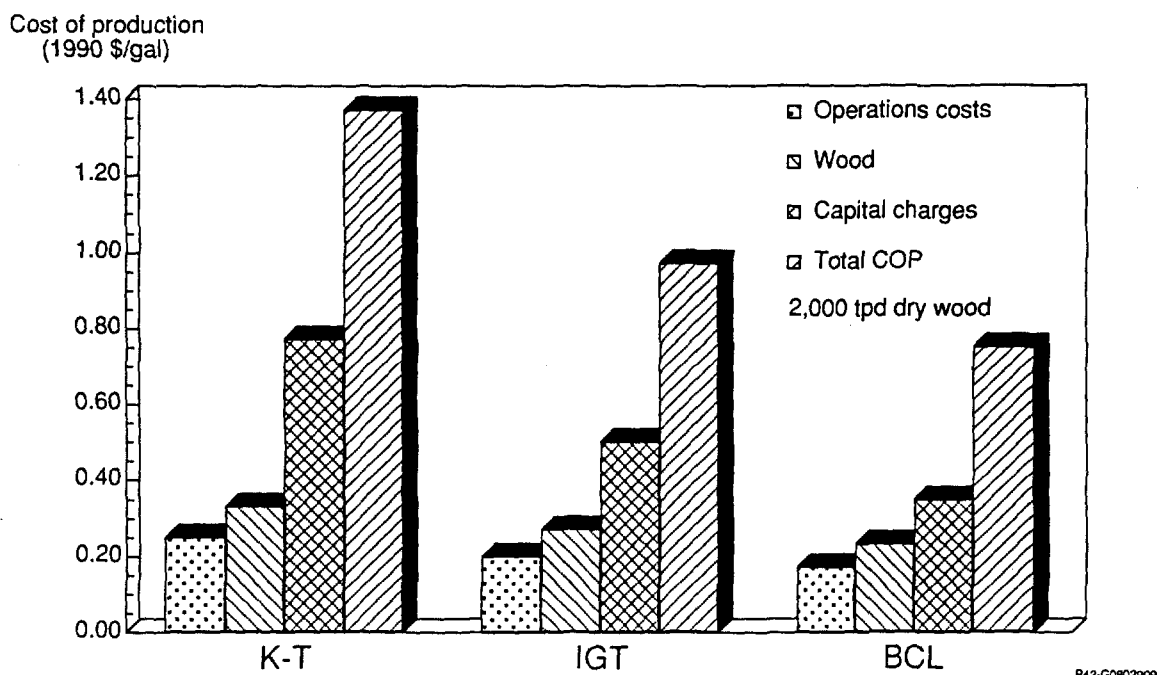


Figure 3. Effect of technology improvements in the projected price of methanol

is expected to contain significantly different impurities and levels of tar than those observed in raw biomass syngas. In addition to these differences, the severity of tar cracking, and hence tar composition, will be different when gasifiers are operated under different conditions. It is therefore important that catalytic syngas conditioning processes be operable over a wide range of realistic conditions.

Laboratory-scale catalytic syngas conditioning experiments are being conducted in continuous flow systems to evaluate operating parameters, including the reaction networks and important kinetics. The overall goal is to improve catalyst lifetimes and optimize catalysts and conditions for raw syngas processing. These experiments will use the MBMS system and a continuous flow microcatalytic reactor system equipped with gas chromatographic product analysis. Initially, a synthetic raw biomass syngas will be formulated from hydrogen, carbon monoxide, carbon dioxide, methane, and polynuclear aromatic hydrocarbons. This will be used as feed for catalytic conditioning experiments on both the MBMS and continuous flow systems. The polynuclear aromatic compound fraction will be formulated to include tar components previously determined to be important. Synthetic gas compositions are varied systematically to study syngas conditioning requirements for various biomass gasifiers and operating conditions. A revised catalyst testing protocol to select the best catalyst will be developed based on these results.

In order to complement the existing laboratory work and to obtain more detailed information on the nature of the contaminants in a large-scale indirect gasifier, a request for proposal (RFP) was issued in FY 1991 for the evaluation and operation of an indirectly heated biomass gasifier process development unit (PDU) at the 0.5-2.5 tph (ton per hour) scale, including incorporation of a slipstream hot gas conditioning train. The contract award was made in December 1991.

The air or oxygen blown gasifier technology is also being scaled up at a site on the island of Maui. The conservation and renewables utility program is cost-sharing with the Pacific International Center for High Technology Research (PICHTER) the scaleup of the IGT Renugas biomass gasifier (from 10 tpd to 100 tpd) as part of the development of advanced gasifier and gas turbine technology. In a later phase of scaleup of the catalytic gas conditioning, it will be necessary to run the units at a biomass feedstock scale of at least 50 tpd prior to full-scale operation. An early possibility is to use the DOE/PICHTER unit to prove this technology before commercialization.

CONVERSION OF BIOMASS FAST PYROLYSIS VAPORS TO REFORMULATED GASOLINE COMPONENTS

The gasoline market is changing rapidly with respect to the desired composition for high performance in the engine, cleanliness of combustion, and minimal adverse impact on the environment. An example of a nearly completed change to the gasolines of the United States is the mandated removal of lead compounds from the gasoline pool, which was driven by

environmental concerns. In progress at this time is the lowering of the vapor pressure of gasoline by the reduction of butane and other volatile compounds in the gasoline pool, with the intent of lowering the evaporative losses from the gas tank. This has resulted in a surplus of butane at the refineries, which conveniently can be converted at the refinery to methyl tertiary butyl ether (MTBE). The MTBE is added back into the gasoline pool as a high octane additive and as a source of bound oxygen, which is thought by many to result in cleaner combustion. MTBE is completely compatible with gasoline and the existing infrastructure.

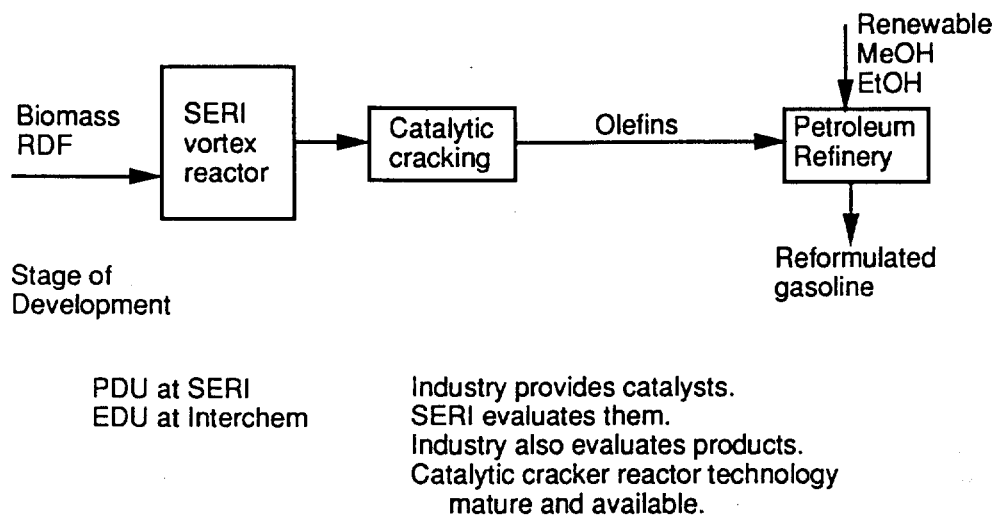
As an added bonus, the use of high octane MTBE in the gasoline pool allows the refiner to operate the refinery in a less severe way, making more gasoline from a given amount of crude oil and using less energy overall. The gasoline made at less severe conditions naturally has a lower aromatic content. This evolutionary change in the composition of gasoline has successfully integrated oxygenated compounds into the gasoline pool of the United States, where several years ago oxygenated compounds were prohibited from gasoline.

Thus far, the ability of the refiners to make reformulated gasoline is quite limited. If all of the butane that was in the mid-1989 gasoline pool were to be converted to MTBE and the MTBE blended back into the gasoline, the resulting reformulated gasoline would contain only 4% MTBE. In those areas affected by the Clean Air Act, a 2.7% oxygen content is mandated, which corresponds to 15% MTBE in the gasoline. Consequently, with the current trend of reformulated gasolines, there will need to be a large increase in the production of oxygenated and paraffinic fuels, along with a decrease in the production of aromatics (especially benzene) and olefinic gasolines (Vervalin 1991).

Thus, the challenge of this task is to develop economically feasible chemical process routes using biomass as the feedstock to produce key components of the reformulated gasolines of the future. Of particular interest are oxygenates, which the petroleum refiners can use, but which they have not historically made (Corbett 1990).

The approach is the fast pyrolysis of biomass to maximize the formation of oxygenated crude oil vapors, which are promptly catalytically cracked to intermediate compounds. The intermediate compounds are then converted to the desired RGCs in an additional but already commercially proven catalytic stage with renewable methanol and ethanol as the co-reactants. This concept is shown in Figure 4, which illustrates how the biomass pyrolysis program can be linked with the existing oil refinery structure.

CURRENT STATUS - The fast pyrolysis of biomass to the oxygenated crude oil vapors has been demonstrated at NREL in a small reactor, normally operated at about 50 lb of dry biomass per hour. This process requires very rapid heating of the biomass to achieve the temperatures at which the predominant pyrolysis reactions form oxygenated crude oil vapors, rather than char, water, or gases. This reactor has a unique vortex flow of the biomass particles, which results in



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Figure 4. Biomass olefins for petroleum refineries

the forced sliding of the biomass particles on the externally heated reactor wall. This sliding contact results in such high rates of heat transfer that the surface of the biomass particle is pyrolyzed and removed, while the bulk of the particle is still unheated, i.e., an ablative pyrolysis phenomena. The development of this vortex reactor at NREL has been described by Diebold and Scabill (1988). Based on first principles and experimental data, the theory of the vortex reactor used for biomass pyrolysis was reported by Diebold and Power (1988).

The conversion of the oxygenated crude pyrolysis oil vapors produced in the vortex reactor by thermal cracking has been studied extensively and was found to yield some olefins and other hydrocarbons of interest, but not enough to be economically interesting. The use of zeolite catalysts to crack the pyrolysis oil vapors has been studied at NREL with HZSM-5 catalyst supplied through a cooperative agreement with Mobil. This is the same catalyst that Mobil uses to convert methanol to gasoline. The dramatically increased yields of olefins using catalyst technology has led to the development of the PYROCAT technology shown in Figure 4.

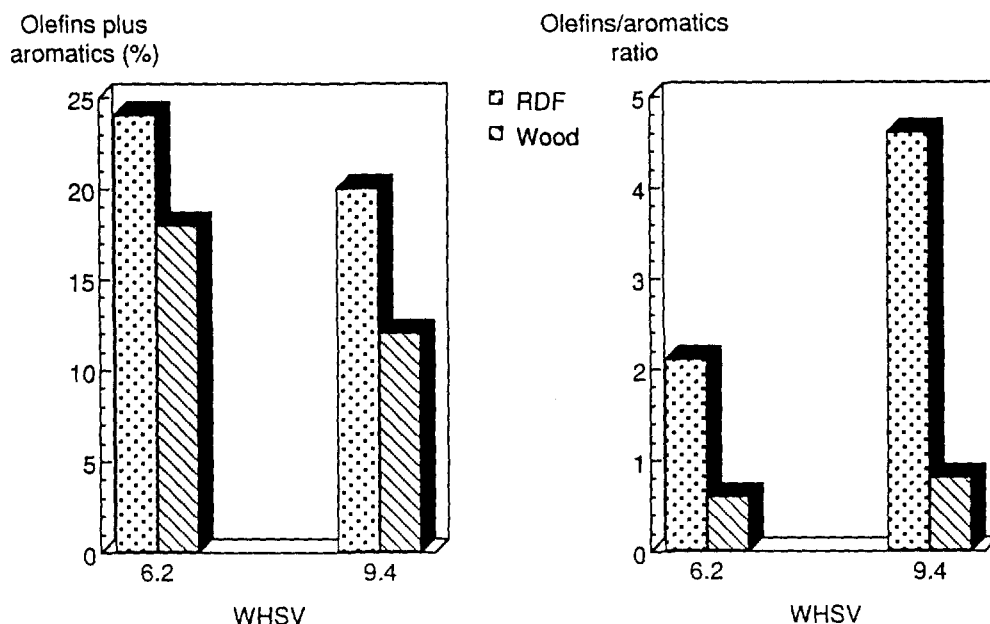
The use of this catalyst with biomass pyrolysis vapors was initially evaluated using NREL's MBMS with a microreactor using 1 g of catalyst. The ongoing research has also used a small, 100-g, fixed-bed, slipstream catalytic cracking reactor at atmospheric pressures. This small reactor was fed pyrolysis vapors directly from the vortex reactor. Researchers at NREL have identified operating conditions with the Mobil catalyst in the slipstream reactor, which result in low coke yields and relatively high yields of high octane alkylated aromatics and some gaseous olefins. This produces a very high octane blending stock, compatible with the current concepts of reformulated gasoline. Preliminary results of these efforts have been reported by Evans and Milne (1988) and by Diebold and Scabill (1988). More recent results with the slipstream reactor were presented in early 1991 at the Institute of Gas

Technology (IGT)-sponsored conference Energy from Biomass and Wastes XV (Rejai et al. 1991). Quite recently, a large, fixed-bed primary catalytic reactor capable of containing 10 kg of catalyst was designed, fabricated, and installed. This large catalytic reactor was successfully fed the entire output of the vortex pyrolysis reactor. This represents a scaleup at NREL of four orders of magnitude relative to the 1-g catalytic reactor used for the MBMS studies.

As noted above, a scarcity of olefins is projected in the future for the production of oxygenated hydrocarbons, such as MTBE, ethyl tertiary butyl ether (ETBE), and higher alcohols. The offgas from the catalytic cracking reactor contains a considerable amount of gaseous olefins. The recovery of these gaseous olefins through catalytic conversion to larger hydrocarbons, which are easier to condense and recover, has been studied with a secondary catalytic reactor sized to the slipstream primary reactor. A small compressor is used to pressurize the offgases to a little under 100 psia. The pressurized gases then enter the secondary catalytic reactor. The potential for the recovery of the gaseous olefins, primarily as isoparaffins boiling in the gasoline range, has been demonstrated. Other catalysts, coreactants, temperatures, and pressures could change the products from the secondary reactor to oxygenated compounds as shown in Figure 4 on the PYROCAT process.

Preliminary technoeconomics of the PYROCAT process are encouraging, especially in the case of RDF, which is a low-cost feedstock that gives enhanced yields of olefins. The increased olefin yield from RDF compared to that from wood is shown in Figure 5. The anticipated yield of mixed ethers and aromatics using today's commercially available catalysts is about 80 gal/ton of RDF, as shown in Table 1.

The research into new catalysts will increase both the olefin yield and the selectivity toward olefins versus aromatics.



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Figure 5. Yields from RDF versus wood

Table 1. Projected "Present" Yields of Methyl Ethers

Per Ton of As-received RDF	
Methanol Consumed	24.1 gal
Products	
MTBE	32.0
TAME	43.6
Toluene	1.7
Xylenes	0.6
Cumene	1.3
Total Products	79.2 gal

Early laboratory screening has already identified some promising candidates. It should be possible to go from today's yield of 80 gal of 95% mixed ethers, having an oxygen content of 15.9%, to a stoichiometry of

34 gal MeOH + 1 ton of RDF olefins =
119 gal of 90% mixed ethers at 15% O.

The use of renewable ethanol to produce ethyl ethers is also possible, and with the projected improved catalysts, we anticipate a stoichiometry of

49 gal MeOH + 1 ton of RDF olefins =
133 gal of 91% mixed ethers at 13% O.

Very preliminary economics of the advanced catalytic process shown in Figure 6 suggest that the mixed ether would have a cost of production of \$0.67/gal as compared with today's estimate of \$0.96/gal. The assumed capital investment

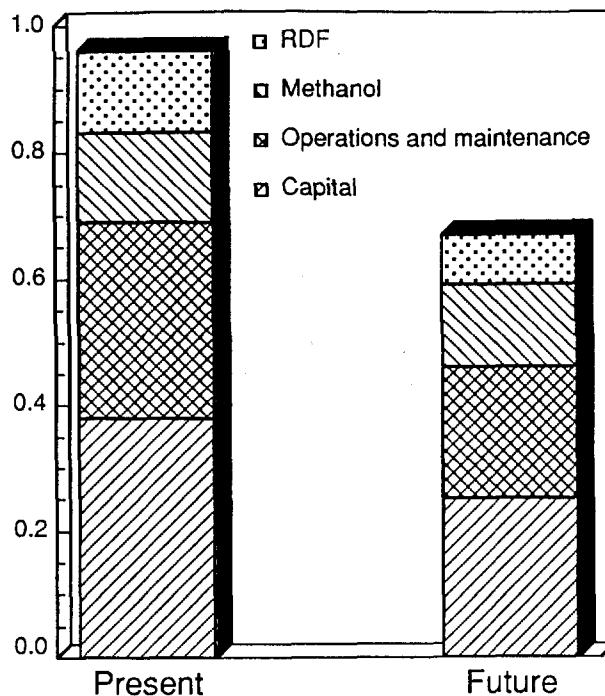
is \$51 million and the cost of the RDF is estimated to be \$10/ton, while that of the methanol is \$0.45/gal.

The catalyst screening is continuing at the MBMS level to explore selectivity and catalyst life. The engineering-scale catalyst reactors are being operated to generate RGCs for testing.

The ability to scale up the fast pyrolysis of biomass to produce condensable pyrolysis vapors has not yet been demonstrated at more than about 200 lb/h. A small business is scaling up NREL's vortex reactor to an announced scale of 3000 lb/h, and is collaborating with NREL to incorporate the design principles developed over a 10-year period in the laboratory and pilot plant. The vortex reactor represents a new technology, which has a considerable risk because of the lack of current industrial experience. With the interaction of the experienced NREL personnel with this small company, the chances for a successful scaleup are greatly enhanced.

FEEDSTOCK/THERMOCHEMICAL PROCESS INTERACTION

The objective of this task is to assess available and developing lignocellulosic feedstocks to select the best candidates for conversion into fuels through thermochemical routes. Literature is being searched and experimental data are being generated for representative feeds that have the potential to supply, on a concentrated regional or national basis, a significant fraction of our energy needs (roughly 3 quads per selected feed). Integral to the selection is the assessment of the environmental acceptability of the feedstock as a sustainable basis for fuels production.



Present

1000 tpd RDF → 26.4×10^6 gal/yr
@ 21.8% ash

Future

1000 tpd RDF → 39.7×10^6 gal/yr
@ 21.8% ash

Estimated capital cost ≈ \$51 million

Capital cost – annual recovery = 20%

Methanol @ 45¢/gal

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Figure 6. Cost of mixed ethers from RDF and MeOH

Because biomass production is seasonal and regional there will be a need to store feedstocks for a certain length of time, depending on the size of the conversion facility, its location, and the number of feedstocks that it will be able to utilize on a given location. Upon storage, these various feedstocks undergo both mass and compositional changes that affect the yield of the fuels produced. These changes need to be quantitatively assessed as a function of season, harvest mode, and storage time. Appropriate models can be generated when this interaction is quantified. In these models, the cost of the feedstock will be correlated with compositional and mass changes (quality) when stored (function of time, location of storage, type of storage, plantation site, harvest type and season, among other factors). Using these models, it will be possible to more quantitatively assess the cost of the production of the feedstocks, which is corrected by that of storage for the appropriate feeds, and thus more correctly assess the overall costs of biofuels production. Factors such as which feedstocks are most suited to specific conversion processes will also emerge. These factors have an impact on the overall selection of production/conversion routes.

This task is a major joint effort of all U.S. DOE Biofuels Program components, including both production and conversion technologies. It is the interface activity applied to thermochemical processes for fuels. It involves a number of subcontractors engaged in various activities such as field operations and analytical chemistry of these feedstocks, laboratory managers both in production and conversion, and consultants.

CURRENT STATUS - NREL began the evaluation of the quality of a variety of feedstocks for thermochemical conversion into fuels in 1989-90, in collaboration with Oak Ridge National Laboratory (ORNL) and the University of Hawaii. The initial efforts concentrated on developing analytical methodology to allow very fast screening of these various feedstocks. The thermochemical methodology for selected pyrolysis/catalysis has been developed, and it will be used to develop quantitative models for the assessment of the interaction between feedstock production, storage, and conversion into selected thermochemical fuels.

Currently eight feedstocks have been selected for study and are being employed in the first round of feedstock evaluation. The selected feedstocks include four woody species (hybrid poplar, American sycamore, black locust, and eucalyptus), two herbaceous species (switchgrass and *Sericea lespedeza*), and two agricultural residues (corn stover and sugar cane bagasse). The procurements for the feed are in place and their analyses are being conducted on a continual basis.

ENVIRONMENT, SAFETY, AND HEALTH ASSURANCE - Liquid transportation fuels from biomass offer significant potential for production of acceptable fuels through safe and environmentally acceptable processes. It is essential that environmental issues be considered during process development in an integrated way that encompasses the complete fuel cycle from biomass production to end product use. By dealing with environmental issues at the earliest

possible time, it should be possible to avoid and ameliorate potential problems prior to scaling up the technology.

These environmental issues range from complying with existing Occupational Safety and Health Administration (OSHA) and Environmental Protection Agency (EPA) regulations through to examining a future in which the greenhouse gases produced during processing are recycled to minimize their effects on the global climate.

RECYCLING THE CO₂ REJECTION STREAM FROM THERMOCHEMICAL METHANOL PRODUCTION

During the thermochemical production of methanol from biomass, a significant fraction of the carbon, typically 40% to 60%, is rejected into the atmosphere as carbon dioxide. Much of this waste carbon dioxide could be utilized by reducing it to carbon monoxide and reinjecting it back into the thermochemical production unit. Thus, methanol production would be enhanced, and loss of carbon dioxide (a gas known to contribute to the greenhouse effect) would be minimized.

As a part of NREL's research for the Office of Energy Research (OER) Basic Energy Sciences program, a new class of catalysts for the electrochemical reduction of carbon dioxide has been developed. These catalysts operate efficiently (i.e., at relatively low overvoltages and with high turnover rates). This program's primary focus is the development of new classes of catalysts and the elucidation of structural factors important in obtaining catalysts with high turnover rates, high selectivity, and long lifetimes. However, for these catalysts to have potential for practical applications, either water-soluble analogs of these catalysts must be prepared and their catalytic activity in water demonstrated, or the surfaces of electrodes must be modified with suitable catalysts.

The program is addressing this important problem in the thermochemical production of methanol by building on the basic research strength developed under the OER program.

CURRENT STATUS - A new class of catalysts, soluble in various organic solvents, has been developed for the electrochemical reduction of carbon dioxide to carbon monoxide. Catalysts soluble in water or attached to electrode surfaces, as needed for application to methanol production, have not been developed and are the subject of the research program.

AIR AND WATER EMISSIONS AND OCCUPATIONAL HEALTH

Several environmental issues need to be addressed for thermochemical conversion processes. In these systems, minerals in the biomass are separated as ash, presenting potential disposal problems. In addition to ash, incompletely reacted char may also be present. Therefore, both ash and char characteristics must be considered.

If wastewaters from biomass conversion processes are present, environmental concerns dictate that the process should be optimized by minimizing these emissions to the biosphere. Also, it would be helpful to understand the chemical nature of these contaminated waters to be able to direct remediation efforts. To date, the wastes have not been carefully characterized, and only a limited amount of work on disposal has been conducted. Research is needed to define required treatments for process wastewater streams and to understand the process operation fully to minimize waste streams.

Other emissions such as tars and nitrogen oxides also need to be monitored as the technologies develop. Although past studies have indicated that these substances do not present major problems, continued analysis will ensure acceptance in these areas. By continuing environmental studies, the program can ensure that there are no major barriers to overcome after technology development.

CURRENT STATUS - Research projects over several years have addressed various environmental issues. Ash handling and disposal have been discussed in a general way, but the specific ash produced in biomass methanol systems has not been well characterized. Similarly, general research has been performed on biomass wastewaters, but specific research on thermal alcohol technologies has not been performed. Technology-specific research in the areas mentioned above is needed to ensure that these processes will be environmentally acceptable as they are developed. The ongoing research strategy is to continue to characterize ash, char, and scrubber liquids from biomass gasifiers and pyrolyzers, looking at the relationship between reactor operating conditions and environmental characteristics of the reactor byproducts. The research will also address problems with DOE co-funded reactor scaleup if needed.

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